

CLAIMS

1. A three-dimensional polymeric coordination compound characterized by a plurality of sheets comprising a two-dimensional array of repeating structural units, each repeating structural unit comprising at least one transition metal atom
5 coordinated to:

- a) one binding site of an exodentate bridging ligand; and
- b) at least one binding member of a bidentate binding site on each of two polyfunctional ligands,

wherein: (1) at least one binding member of a second bidentate binding site on
10 each said polyfunctional ligand is further coordinated to at least one transition metal atom in a different repeating structural unit within the same said sheet containing a two-dimensional array of repeating structural units; (2) the exodentate bridging ligand extends essentially perpendicularly from a plane characteristic of said sheet containing a two-dimensional array of
15 repeating structural units to further coordinate with a transition metal atom in a repeating structural unit in an adjacent sheet; (3) the polyfunctional ligand is a ligand having at least two bidentate coordination sites; and (4) the exodentate ligand is a ligand having two monodentate binding sites,

wherein the polyfunctional ligand compounds and the exodentate ligand
20 compounds are selected so that (i) substitution of the exodentate ligands is more facile than substitution of the polyfunctional ligands by a ligand having a single, monodentate coordination site, and (ii) the ligands of the three-dimensional polymeric compound define channels and pores of molecular size throughout the structure of the compound.

25 2. The compound of claim 1 wherein the repeating structural unit of the compound has the stoichiometric formula $[M_a(\text{pbd})_b\text{ed}_c] \cdot x(\text{sol}) \cdot z \text{H}_2\text{O}$, where "M" is a transition metal selected from the group of transition metals having in at

least one stable oxidation state classified as a Pearson soft or borderline acid, and which, in some oxidation state, can form stable bonds with ligands selected from the group consisting of ligands classified as Pearson hard bases and ligands classified as Pearson borderline bases, "pbd" is a polyfunctional ligand having at least two bidentate binding sites, "ed" is an exodentate ligand having at least two monodentate binding sites, sol is one or more members of the group selected from polar solvents, "a" and "b" are integers and the coordinate space occupied by the pbd and ed ligands is equal to a stable coordination number of "a" number of M transition metal atoms, and wherein "x" and "z" are any number of solvent molecules including zero.

3. The compound of Claim 2 wherein "M" is cobalt, "pbd" is biphenyl-4,4'-dicarboxylate, "ed" is 4,4'-bipyridine "sol" = dimethyl formamide, "a" and "b" = 3, "f" = 1, "x" = 4, and "z" = 1, the compound being further characterized in that the three cobalt atoms of the repeating structural unit are arranged such that one octahedral coordinate cobalt atom resides between two cobalt atoms having trigonal bipyramidal coordination, the octahedral ligands comprising one oxygen atom (a binding member) of a bidentate binding site of each of six biphenyl- 4, 4'-dicarboxylate polyfunctional ligands, the trigonal bipyramidal ligands comprising one oxygen atom of a bidentate binding site of each of two biphenyl- 4, 4'-dicarboxylate polyfunctional ligands, two oxygen atoms of one additional bidentate binding site of a biphenyl- 4, 4'-dicarboxylate polyfunctional ligand, and the nitrogen of one monodentate binding site of a 4, 4'-bipyridine exodentate ligand.

4. A method for preparing a pillared porous polymeric coordination compound having the stiochiometric formula $[\text{Co}_3(\text{bpdc})_3(\text{bpy})]\cdot 4(\text{DMF})\cdot (\text{H}_2\text{O})$, where (bpdc) is a biphenyl- 4, 4'-dicarboxylate polyfunctional ligand, bpy is a 4, 4'-bipyridine exodentate ligand, and DMF is dimethylformamide, comprising contacting a polymeric precursor compound of the stiochiometric formula $[\text{Co}(\text{bpdc})(\text{H}_2\text{O})_2]\cdot (\text{H}_2\text{O})$, where (bpdc) is a biphenyl- 4, 4'-dicarboxylate polyfunctional ligand, with bipyridine under solvothermal ligand-replacement conditions.
5. A process for the synthesis of a pillared porous polymeric coordination compound of the stiochiometric formula: $[\text{M}_3(\text{pbd})_3\text{ed}]\cdot x \text{ DMF} \cdot z \text{ H}_2\text{O}$, where M is a transition metal selected from the group of transition metals having in at least one stable oxidation state classified as a Pearson soft or borderline acid, and which, in some oxidation state, can form stable bonds with ligands selected from the group consisting of ligands classified as Pearson hard bases and ligands classified as Pearson borderline bases, "pbd" is a polyfunctional ligand having at least two bidentate binding sites, "ed" is an exodentate ligand having at least two monodentate binding sites, and wherein "x" and "y" are selected independently to be any number of solvent molecules including zero, comprising contacting a compound of the stiochiometric formula $[\text{M}(\text{pbd})(\text{H}_2\text{O})_2]\cdot (\text{H}_2\text{O})$ with an ed compound in the presence of dimethyl formamide under solvothermal ligand replacement conditions.
6. The synthesis process of claim 5, wherein "pbd" is biphenyl 4,4'-dicarboxylate, the exodentate ligand having two monodentate binding sites is 4,4'-bipyridine and "M" selected from the group consisting of cobalt and zinc.

7. A process for carrying out a chemical reaction and isolating a product thereof, wherein the reactants are contained during the reaction within a polymeric coordination compound of claim 2, the process comprising:

- 5 (a) containing within the structure of said polymeric coordination compound of claim 2 one or more reactants;
- (b) generating a reactive species from one or more of the contained reactants, thereby causing a reaction that forms one or more of the reaction products; and
- 10 (c) converting, by ligand exchange, the polymeric coordination compound to its lower dimensional precursor compound to the extent that the structure is disrupted sufficiently to liberate one or more of the products of the reaction, the ligand exchange being characterized by a substitution of some or all of the exodentate ligands with ligands having a single, monodentate binding site.

15 8. The process of Claim 7, wherein the pillared polymeric coordination compound has the stoichiometric formula $[\text{Co}_3(\text{bpdc})_3(\text{bpy})] \cdot x \text{ DMF} \cdot z \text{ H}_2\text{O}$ wherein (bpdc) is a biphenyl- 4, 4'-dicarboxylate polyfunctional ligand, "bpy" is 4,4'-bipyridine, "DMF" is dimethyl formamide, and "x" and "z" are selected independently to be any number of solvent molecules including 0.

20 9. The process of claim 7 further comprising the step of treating the polymeric precursor compound with bipyridine under "solvothral" ligand replacement conditions to yield the pillared porous polymeric compound of claim 4.

10. The process of claim 9 further comprising repeating the process from step "a", the containing step.
11. A process for synthesizing a compound of claim 1 comprising contacting an inorganic complex of the formula $M(NO_3)_2 \cdot 6(H_2O)$ with an aliquot of a polyfunctional ligand ("pbd") and an aliquot of an exodentate ligand ("ed") under solvothermal conditions wherein the stoichiometric ratio of said inorganic complex to said pbd ligand is 1:1 and the stoichiometric ratio of said inorganic complex to said exodentate ligand is 1:a, wherein "a" is equal to 1 or 4.
12. The compound of claim 1 wherein the repeating structural unit of the compound has the stoichiometric formula $[M(pbd)ed] \cdot x(sol)$, where "M" is a transition metal selected from the group of transition metals having in at least one stable oxidation state classified as a Pearson soft or borderline acid, and which, in some oxidation state, can form stable bonds with ligands selected from the group consisting of ligands classified as Pearson hard bases and ligands classified as Pearson borderline bases, "pbd" is a polyfunctional ligand having at least two bidentate binding sites, "ed" is an exodentate ligand having at least two monodentate binding sites, sol is one or more members of the group selected from polar solvents, and "x" is any number, including fractions and zero.
13. The compound of Claim 12 wherein "M" is cobalt, "pbd" is biphenyl-4,4'-dicarboxylate, "ed" is 4,4'-bipyridine, "sol" = dimethyl formamide, and "x" = 0.5, the compound being further characterized in that it has a repeating structural unit comprising two cobalt atoms having octahedral coordination, the coordinating ligands comprising four equatorial biphenyl- 4, 4'-

dicarboxylate ligands wherein one oxygen atom (a binding member) of one bidentate binding site of each of two biphenyl- 4, 4'-dicarboxylate polyfunctional ligands is coordinated to each of the cobalt atoms, forming a bridge between said cobalt atoms, and one bidentate binding site of each of two additional biphenyl- 4, 4'-dicarboxylate ligand is coordinated to each cobalt atom, and wherein each cobalt atom of said repeating structural unit is apically coordinated to the nitrogen of one monodentate binding site of each of two 4, 4'-bipyridine exodentate ligands.

14. A method for preparing a pillared porous polymeric coordination compound

having the stiochiometric formula $[\text{Co}(\text{bpdc})(\text{bpy})] \cdot 0.5(\text{DMF})$, where (bpdc) is a biphenyl- 4, 4'-dicarboxylate polyfunctional ligand, bpy is a 4, 4'-bipyridine exodentate ligand, and DMF is dimethylformamide, comprising contacting a two-dimensional polymeric precursor compound of the stiochiometric formula $[\text{Co}(\text{bpdc})(\text{py})_2] \cdot (\text{H}_2\text{O})$, where (bpdc) is a biphenyl- 4, 4'-dicarboxylate polyfunctional ligand and (py) is pyridine, with 4,4'-bipyridine under solvothermal ligand-replacement conditions in a ratio of 1 mole of said precursor compound with 4 moles of said bipyridine.